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EFFECT OF VARIOUS FACTORS ON THE RATE OF REDUCTION OF ZINC FERRITE, CALAMINE, AND WILLEMITE BY CARBON.

-By-

Foster Cary Nix.

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

DEGREE OF

MASTER OF SCIENCE.

Rolla, Missouri,

1925.

Approved: B. M. O'Harra

Acting Superintendent of the Mississippi Valley Experiment Station of the U. S. Bureau of Mines.

29938

T A B L E O F C O N T E N T S.

L I S T O F I L L U S T R A T I O N S.

EFFECT OF VARIOUS FACTORS ON THE RATE OF REDUCTION OF ZINC FERRITE, CALAMINE, AND WILLEMITE BY CARBON.

-By-

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INTRODUCTION.

Zinc ores containing large amounts of ferric oxide, calamine and willemite have been known for a long time among practical zinc metallurgists to be more difficult to reduce than ores of the same type but free from the above named compounds. This has been thought to be due to the high temperatures necessary for the reduction of the zinc ferrite and the zinc silicates by carbon. The ferrite is formed both during the roasting of sulphide ores and during distillation in the retorts, while calamine and willemite are introduced as such in the ores. The amount of ferrite formed during the roasting process depends almost entirely upon the temperature at which the roast is conducted, as excessively high temperatures are conducive to the formation of the ferrite. The object of the investigation described in this thesis was to determine the effect of various factors on the rate of reduction of zinc ferrite, willemite,

and calamine, in order to obtain more specific data concerning the reasons for the difficulty of reducing ores containing large amounts of these compounds.

A SUMMARY OF THE INFORMATION FOUND IN THE LITERATURE ON ZINC FERRITE AND ZINC SILICATES.

Very little information is to be found in the literature concerning the physical and chemical properties and reducibility of zinc ferrite, willemite, and calamine. Following is a brief summary of the information found:

Zinc Ferrite.

Physical and Chemical Properties:

The composition of zinc ferrite has been determined[1] by various researches and found to conform to the atomic proportions of $ZnFe_2O_4$.

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[1] Hofman, H. O., Metallurgy of zinc and cadmium, New York, McGraw-Hill Book Co., 1922; p. 44.

Hamilton, E. H., Murray, G., and McIntosh, D., The formation of zinc ferrate, Trans. Canad. Min. Inst., Vol. XX, 1917, pp. 168-179.

Frost, E., Bull. Assoc. Belge. Chem., 1896, Vol. X, p. 246; Abst., Min. Ind., 1896, Vol. V, p. 596.

According to the strict nomenclature of inorganic chemistry the ferrite is a salt of the hypothetical ferrous acid $HFeO_2$.

Zinc ferrite crystals[2] form in the octahedral system, are black and very brilliant. They have a hardness of slightly above feldspar on the Mohr scale, are slightly magnetic and have a specific gravity of 5.13.

Notes on the Formation of Zinc Ferrite During the Roasting Process and its Effect on Ensuing Metallurgical Operations.

Hommel[3] concluded from observations made in practice that "The formation of zinc ferrite only takes place in the roasting furnace when the blende is heated excessively from the outside and the sulphur burns under conditions favorable for the generation of a maximum of heat. In this case the temperature requisite for the formation of the ferrite will always be locally produced. That this temperature lies above 1200° C. seems to follow from the experience had in zinc smelteries, that if well roasted ferruginous blende is distilled at too high a temperature great losses will result in consequence of ferrite formation in the muffle."

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[2] Wells, J. C. S., The ferrite compounds of an iron acid, Eng. & Min. Jour., Vol. 86, 1908; pp. 420-422.

[3] Hommel, W., The principles of blende roasting, Metallurgie, Vol. 9, May 8, 1912; pp. 281; Abst.; Eng. & Min. Jour., Vol. 94, 1912; pp. 697-700.

This observation must be supplemented by the admonitions of Lindt,[4] that the zinc metallurgist must not only direct his attentions toward the ferrite in roasting, but also toward the ferrite formed in the muffle of the retort.

The conclusions reached by Mostowitsch[5] were that the ferrite of zinc forms at a temperature above 700° C.

A method very much used[6] for the preparation of zinc ferrite in the laboratory is to heat ferric oxide with zinc sulphate in an assay muffle; at relatively low temperatures this method yields large percentages of the ferrite. This result is in accord with the conclusions reached by the above mentioned observers.

The probable reaction that takes place in the above process is,

$$ZnSO_4 + Fe_2O_3 = ZnFe_2O_3 + SO_3$$

The SO_3 breaks down into SO_2 and O at the temperatures of the reaction. Another method for preparing the ferrite in the laboratory is to heat iron sulphate together with zinc oxide in the same fash-

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[4] Lindt, V., Untersuchungen über das zinkoxyd im calcinierten galmei und in gerösteter blende, Metallurgie, Vol. 6, 1909; p. 75.

[5] Mostowitsch, W., Zinc sulphate behavior at high temperatures, Metallurgie, Vol. 8, 1911; pp. 763-791. Abst.; Jour. Soc. Chem. Ind., Vol. 31, 1912; p. 76.

[6] Brooks, G. S., Notes on the formation of ferrites in the roasting of blende, Trans. Amer. Inst. Min. Met. Engr., Vol. 45, 1913; pp. 210-25.

ion as in the above case. However, it is very probable that the formation of zinc ferrite in practice does not occur by the chemical combination of ferric sulphate with zinc oxide, the reason being that iron has little tendency to form the sulphate at the working temperatures of zinc roasting furnaces. It has been suggested that the reaction might be made possible by the conversion of either the iron or the zinc for a moment into the nascent condition as their desulphurization proceeds, but the facts that the oxides themselves combine on heating makes this assumption less plausible.

It is most probable that the ferrite is formed in practice by the combination of the oxides of the two metals, or the sulphate of the zinc with the oxide of the iron, or by the desulphurisation of any zinc iron mineral present. Brooks found that when the two oxides, in a finely divided condition, were heated together they did not form the ferrite to any appreciable extent, notwithstanding some of the earlier observers to the contrary.

Zinc Silicates.

Willemite.

Willemite[7] is a zinc silicate mineral having a composition corresponding to the atomic proportions, Zn_2SiO_4. It is apple green in color, and crystallizes in the hexagonal system; the crystals usually contain from 1.5 to 3.0 per cent manganese. In the pure state the zinc content is 58.61 per cent.

Rogers[8] states that willemite has been found varying in color from pale red, yellow, to green and having a specific gravity of 4.1 and a hardness of 5.5.

Calamine.

Calamine[9] is a hydrous silicate mineral of zinc having a white color with a slightly bluish to greenish shade, crystallizing in the orthorhombic system and having a vitreous luster. Rogers[10] gives a composition corresponding to the formulae $2\ ZnSiO_2 \cdot H_2O$, a hardness of 5 and a specific gravity of 3.4.

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[7] Hofman, H. O., Metallurgy of zinc and cadmium, New York, McGraw-Hill Book Co., 1922; p. 50.

[8] Rogers, A. F., Study of minerals, New York, McGraw-Hill Book Co. p. 414.

[9] Hofman, H. O., Metallurgy of zinc and cadmium, New York, McGraw-Hill Book Co., 1922;

[10] Rogers, A. F., Study of minerals, New York, McGraw-Hill Book Co., p. 405.

EXPERIMENTAL INVESTIGATION.

The purpose of the experimental investigation to be described was as noted in the introduction, to determine the effect of various factors on the rate of reduction of zinc ferrite, willemite, and calamine.

The investigation included several groups of experiments to determine the effect of the following three factors upon the rate of reduction of each of the above compounds:

A. Temperature.

B. Time.

C. Physical character of reducer.

The different groups of experiments will be discussed separately. Each group consisted of numerous individual experiments in which all conditions except that whose effect was being studied were kept as nearly constant as possible.

The materials used in the investigation had the following analyses:

Zinc ferrite:

Zinc (total)	-	24.3 per cent
Zinc (uncombined)	-	0.26 per cent
Iron	-	45.90 per cent.

Calamine:

Zinc	-	51.81	per cent
Silica	-	25.70	per cent
Iron	-	0.49	per cent
Lime	-	0.0	per cent
Lead	-	0.0	per cent
Manganese	-	0.0	per cent

Willemite:

Zinc	-	48.31	per cent
Silica	-	24.02	per cent
Iron	-	1.74	per cent
Lime	-	1.02	per cent
Lead	-	0.0	per cent
Manganese	-	5.21	per cent
Sulphur	-	0.31	per cent

Coke:

Fixed carbon	-	84.50	per cent
Volatile matter	-	1.78	per cent
Ash	-	13.12	per cent
Moisture	-	0.60	per cent
Sulphur	-	1.24	per cent

Anthracite Coal:

Fixed carbon	- 75.72	per cent
Volatile matter	- 7.46	per cent
Ash	- 13.99	per cent
Moisture	- 2.83	per cent
Sulphur	- 0.98	per cent

The zinc ferrite was prepared in the laboratory by mixing solutions of zinc sulphate and ferrous sulphate in the ratio of 4.97 parts of ferrous sulphate to 1.43 parts of zinc sulphate. This mixture was evaporated to dryness, then roasted in an assay muffle until the sulphur was eliminated. The mixture was then ground in a small pebble mill to ensure perfect mixing, and heated at 1000° C. for a period of three hours. It was then tested for uncombined zinc oxide and sufficient ferric oxide added to combine with the remaining uncombined zinc oxide. This mixture was again ground in a pebble mill and heated at 1000° C. for a period of three hours as before. After this heating the uncombined zinc oxide, which was found to be below one per cent, was leached out with Low's[11] solution and the purified zinc ferrite was dried and ignited to drive off the leaching solution. This procedure gave zinc ferrite con-

[11] Wells, J. C. S., The ferrite compounds of an iron acid, Eng. & Min. Jour., Vol. 86, 1908; pp. 420-422.

taining 24.3 per cent total zinc, 0.26 per cent uncombined zinc, and 45.9 per cent iron, as compared to the 27.11 per cent zinc and 46.3 per cent iron contained in C. P. zinc ferrite. The willemite and calamine used were samples of the natural minerals, the samples selected being as pure as were available.

Method of Conducting the Individual Experiments.

The method of conducting the individual experiments was similar to that used in a previous experimental investigation of the reduction of zinc oxide by carbon[12]. The proportion of the given zinc compound and carbon used in all the experiments was 100 parts of the zinc compound to 50 parts of carbon; if not already finer than 100-mesh the zinc compound and carbon were pulverized to pass a 100-mesh screen. The mixture of zinc compound and carbon, together with five cc. of water, was formed by means of a small hand mold into cylindrical briquets about one inch long and one inch in diameter, weighing about 35 grams. The briquets were firm enough to hold together during distillation if they were carefully handled.

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[12] Zeller, G. A., Reduction of zinc oxide by carbon, Thesis, 1924; Missouri School of Mines and Metallurgy.

Just after the molding of the briquets they were placed in a drying oven which was maintained at a constant temperature of 110° C. for a period of one hour, so as to ensure complete removal of the water. It is probable that the zinc compound was not reduced as rapidly in non-porous briquets, such as these, made of finely divided zinc compound and carbon without binder, as it would have been in a loose mixture with carbon, but it was thought that the intimacy of contact between the zinc compound and carbon, which has an important effect on the rate of reduction, would be more nearly uniform in all experiments if briquets were used. The use of briquets also simplified the accurate weighing of the charge and of the residue after distillation.

Ordinarily about a dozen briquets were made up at one time, and out of such a lot two were taken as samples and were crushed and analysed separately; these analyses were compared with the analyses calculated from the weights of the zinc compound and carbon used for the briquet mixture, as a check upon the uniformity of the briquet mixture and upon the accuracy of the analytical methods.

One briquet was used for each experiment. It was distilled in a graphite retort measuring 1.25 inches in diameter by 2.5 inches deep, inside dimensions, with a wall 0.3 inch thick. The retort cover, a circular graphite disc with a hole in its center just large enough to admit a pyrometer protection tube of porcelain or fused quartz,

and a small hole near one edge to serve as an ixit for zinc vapor and carbon monoxide, was cemented to the top of the retort with hot pitch. The retort was heated in a vertical cylindrical electric furnace; a nichrome wire resistance furnace was used for the experiments at temperatures up to 1000° C., and a furnace with granular carbon resistor[13] for the experiments at higher temperatures. Figure 1 is a diagram of the furnace.

Temperature was measured with a platinum, platinum-rhodium thermocouple, connected to a Leeds and Northrup recording potentiometer. The thermo element was standardized frequently against Bureau of Standards lead, zinc, aluminum and copper. The temperature of the furnace was controlled by an automatic relay and contactor, activated by the Leeds and Northrup recording potentiometer, and controlled within plus or minus 10° C.

The procedure in each experiment was as follows: A weighed briquet was sealed in the graphite retort and the retort placed in the furnace. The end of the thermocouple, with its protectingvtube, was then inserted through a hole in the retort cover until the protecting tube touched the top of the briquet and the recording potentiometer was set for the desired temperature. The time

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[13] Jeffries, Zay, Notes on the gran-annular electric furnace, Chem. & Met. Eng., Vol. 12, 1914; p. 154.

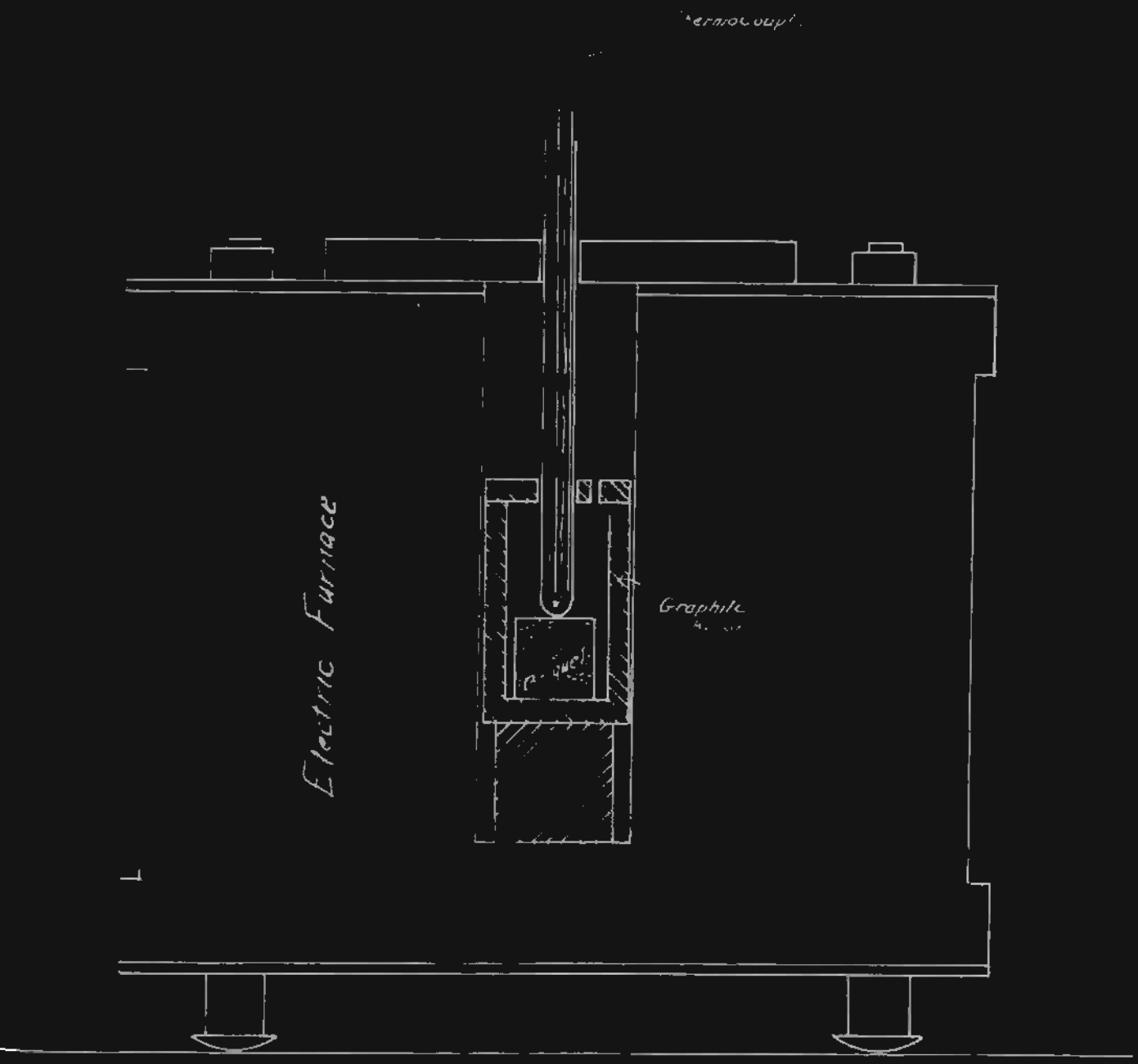
Thermocouple
Electric Furnace
Graphite

Figure 1.

Diagram of Apparatus Used for

Distillation of the Briquet.

was noted and the current turned on. The furnace was heated as rapidly as possible to the temperature at which the experiment was to be run, then the automatic relay and contactor would maintain the temperature constant for the desired time. The time required to raise the temperature of the furnace from 900° C., the temperature at which zinc first begins to be distilled in appreciable amounts, to the final temperature was maintained,as nearly as possible, the same in all experiments except those at final temperatures of less than 1000° C., where this time was proportionately less. From fifteen to twenty minutes were required to heat the nichrome resistor furnace from 900° to 1000° C., and about the same time to heat the carbon resistor furnace from 900° to 1100° C.

At the end of the desired time of distillation the heating current was turned off, the pyrometer quickly removed, the retort taken from the furnace, and a lump of fire clay, "adobe", pressed down upon the retort cover to prevent the ingress of air while the retort cooled. When the retort was cool enough to be handled the cover was removed and the condition of the briquet residue noted; this residue was then weighed, pulverized and analyzed. The zinc contents of the original briquet and of the residue were calculated, and from these the weight of the zinc volatilized was determined. The weight of zinc volatilized was converted to percentage of the weight of zinc contained in the original briquet and tabulated with the results of other experiments.

Effect of Temperature on the Rate of Reduction of Zinc Ferrite by Carbon.

Two series of experiments were carried out to determine the effect of temperature on the rate of reduction of zinc ferrite. In one series coke was used as reduction material, and in the other one anthracite coal was used. Each series consisted of several individual experiments, carried out at small temperature intervals, from the temperature at which the amount of zinc volatilized was negligible in two hours, to the temperature at which complete volatilization of the zinc was obtained. In all the experiments the furnace was held constant at the desired temperature for two hours. The percentages of the original zinc content that were volatilized in two hours at the various temperatures are shown in Table I and Figure 2.

Each of the small circles in Figure 2 represents the results of an experiment with ferrite and anthracite, while the triangles represent the results of the experiments with ferrite and coke. As shown by the curves, the volatilization of zinc, with either reduction material, begins at some temperature below 900° C. and increases with increasing temperatures, slowly at first but rapidly with increasing temperature. After rising rapidly at these temperatures the curves bend over to the right indicating that the rate of reduction is less rapid at still higher temperatures; it is evident, however, that this retardation in the reduction rate is due to the fact that

Table I.

Effect of Temperature on the Rate of Reduction of Zinc Ferrite by Carbon.

Materials	Temperature Degrees C	Time Hours	Zinc Volatilized Per cent of Original Content	
Zinc Ferrite - Coal	800	2	4.12	
Zinc Ferrite - Coal	850	2	3.14	
Zinc Ferrite - Coal	875	2	12.00	
Zinc Ferrite - Coal	900	2	19.32	
Zinc Ferrite - Coal	925	2	41.46	
Zinc Ferrite - Coal	950	2	58.11	
Zinc Ferrite - Coal	975	2	96.02	
Zinc Ferrite - Coal	1000	2	96.97	
Zinc Ferrite - Coal	1050	2	100.00	
Zinc Ferrite - Coke	850	2	0.00	
Zinc Ferrite - Coke	900	2	3.61	
Zinc Ferrite - Coke	925	2	55.00	
Zinc Ferrite - Coke	950	2	29.11	39.01
Zinc Ferrite - Coke	975	2	95.84	99.70
Zinc Ferrite - Coke	1000	2	94.97	
Zinc Ferrite - Coke	1050	2	99.60	

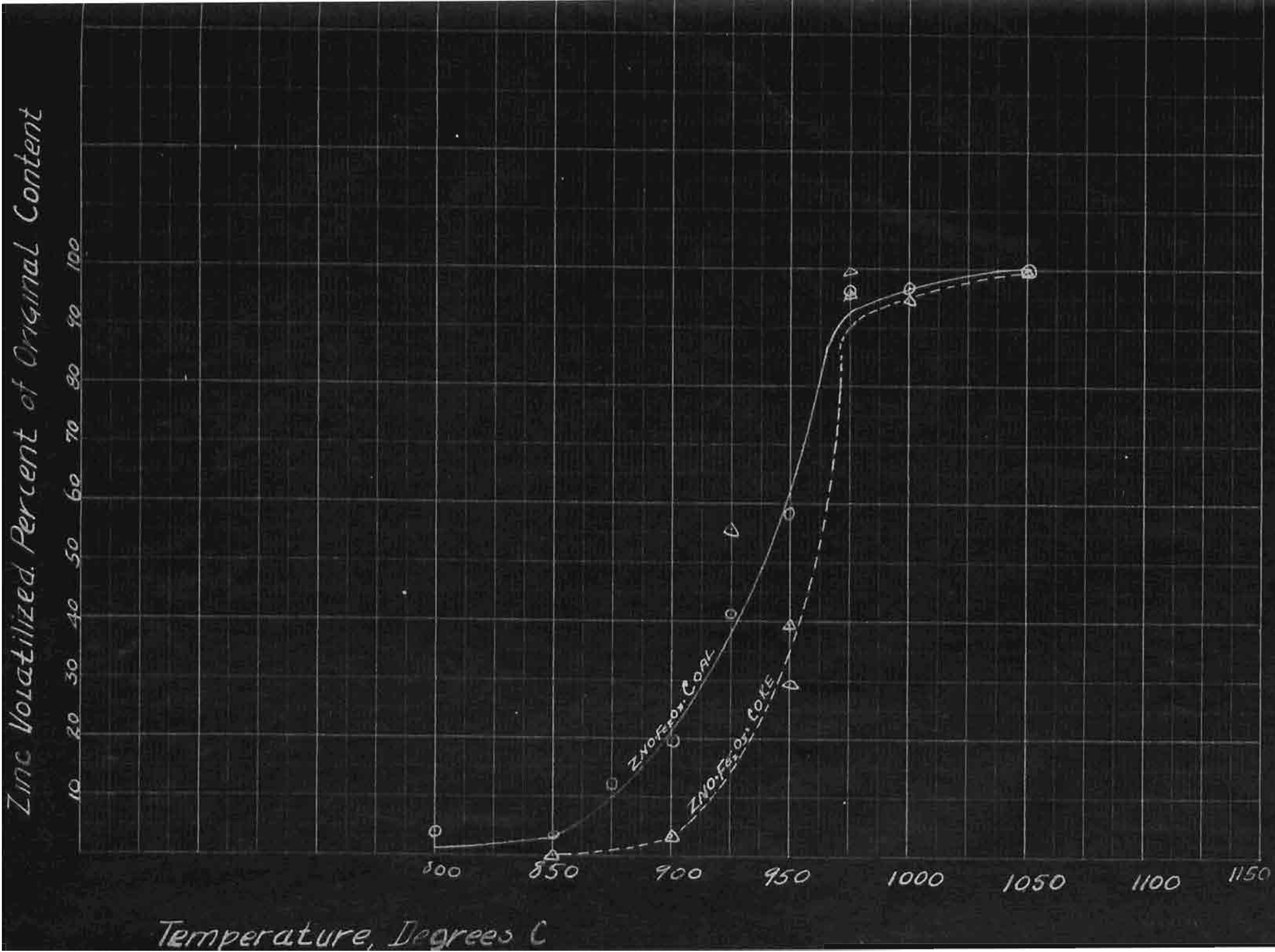
Zinc Volatilized Percent of Original Content
10
20
30
40
50
60
70
80
90
100
800
850
900
950
1000
1050
1100
1150
ZnO.Fe2O3. Coal
ZnO.Fe2O3. Coke
Temperature, Degrees C

Figure 2.

Curves showing the effect of temperature on the rate of reduction of zinc ferrite by carbon.

Time - Two hours in each experiment.

in the experiments at the higher temperatures, the zinc was nearly completely volatilized in the two hours or less, and reduction necessarily slowed down, because of the much diminished amount of zinc present.

The accuracy of the experimental results is not sufficient to determine the exact temperature at which the reduction begins. It is very noticeable that the reduction begins at some temperature below 900° C. It is to be noticed that some zinc was volatilised below 850° C., in the experiments with anthracite coal; this was probably due to the reduction of zinc by the volatile hydrocarbons present, rather than to reduction by elemental carbon.

Effect of Time of Distillation on the Rate of Reduction of Zinc Ferrite.

Two series of experiments, one with zinc ferrite and anthracite coal, and one with zinc ferrite and coke, were carried out to determine the effect of time on the rate of reduction of zinc ferrite.

Each series of experiments included one experiment in which the charge was simply heated to 950° C. to determine the amount of zinc volatilized in heating to that temperature, one in which the charge was heated to 950° C., and held constant for one hour, and others in which the temperature was held constant for two, three, and four hours, respectively. The percentage of zinc volatilized at 950° C. during the various times of distillation are given in Table II and Figure 3.

In the series of experiments on zinc ferrite and anthracite coal, the rate of reduction decreased with increasing time of distillation. The results of the experiments on zinc ferrite and coke were rather erratic. In the case of zinc ferrite and anthracite coal as smooth a curve as possible was drawn between points to show the relation of time of the rate of reduction, while for zinc ferrite and coke a series of straight lines had to be resorted to on account of certain points being off the general trend of the curve.

Table II.

Effect of Time on the Rate of Reduction of Zinc Ferrite.

Materials	Temperature Degrees C	Time Hours	Zinc Volatilized Per cent of Original Content	
Zinc Ferrite - Coal	950	0	1.54	5.24
Zinc Ferrite - Coal	950	1	24.82	
Zinc Ferrite - Coal	950	2	58.11	
Zinc Ferrite - Coal	950	3	80.72	
Zinc Ferrite - Coal	950	4	90.00	
Zinc Ferrite - Coke	950	0	0.114	
Zinc Ferrite - Coke	950	1	28.91	31.65
Zinc Ferrite - Coke	950	2	59.51	29.11
Zinc Ferrite - Coke	950	3	75.74	
Zinc Ferrite - Coke	950	4	89.00	

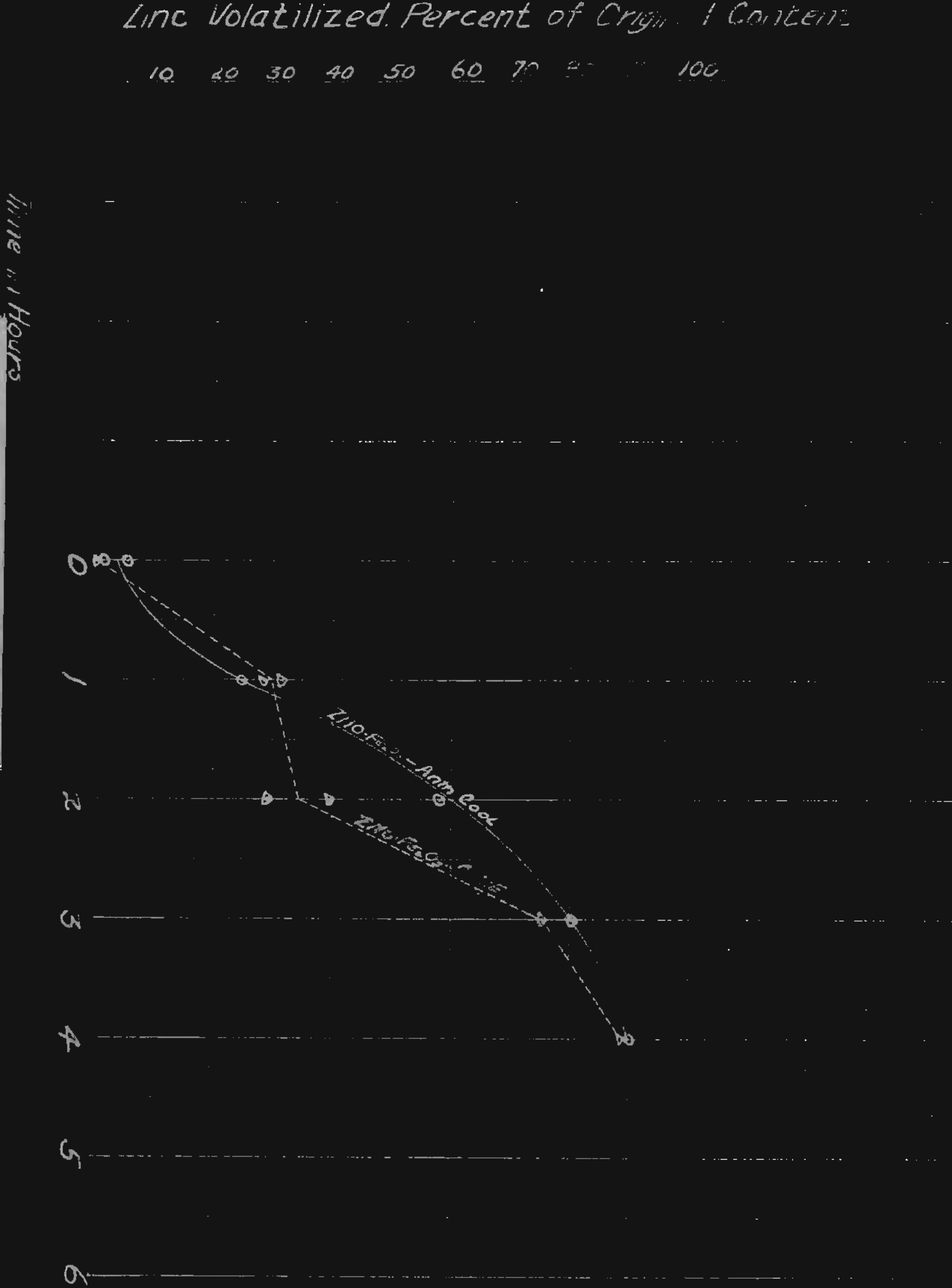
Zinc Volatilized. Percent of Orgn. C Content
10
20
30
40
50
60
70
100
Time in Hours
0
1
2
3
4
5
6
Zinc Ore - Ann Cook
Zinc Ore

Figure 5.

Curves showing the effect of time on the rate of reduction of zinc ferrite by carbon.

Temperature - 950° C. in all experiments.

Effect of Temperature on the Rate of Reduction of Calamine by Carbon.

Three series of experiments were carried out to determine the effect of temperature on the rate of reduction of calamine by different forms of carbon. Calamine was used with anthracite coal, coke, and graphite respectively, as reduction material, in the three series. As in the case of zinc ferrite, each series consisted of several individual experiments carried out at small temperature intervals, from the temperature at which the amount of zinc volatilized was negligible to the temperature at which complete volatilization of the zinc was obtained. The percentages of the original zinc present, that were volatilized in two hours at various temperatures are shown in Figure 4 and Table III.

The same notation is used in Figure 4 as in Figures 2 and 3, with the addition of squares for the experiments on calamine and graphite, that is, circles, triangles and squares were used for the experiments with anthracite coal, coke, and graphite, respectively. The curves are drawn through the points plotted from the respective series of experiments, so as to show the effect of temperature on the rate of reduction, as determined experimentally.

Table III.

Effect of Temperature on the rate of

Reduction of Calamine by Carbon.

Materials	Temperature Degrees C.	Time Hours	Zinc Volatilized Per cent of Original Content			
Calamine - Coal	850	2	3.86			
Calamine - Coal	900	2	7.09			
Calamine - Coal	950	2	17.44	11.74		
Calamine - Coal	1000	2	46.00	54.20	37.19	38.40
Calamine - Coal	1025	2	90.20			
Calamine - Coal	1050	2	99.03			
Calamine - Coal	1100	2	99.82			
Calamine - Coke	850	2	2.96			
Calamine - Coke	900	2	8.95			
Calamine - Coke	950	2	14.38			
Calamine - Coke	1000	2	29.77	37.40		
Calamine - Coke	1025	2	95.39	29.31	61.60	
Calamine - Coke	1050	2	87.90	99.20	89.70	
Calamine - Coke	1100	2	99.94			
Calamine - Graphite	850	2	2.064			
Calamine - Graphite	900	2	0.0			
Calamine - Graphite	950	2	9.17			
Calamine - Graphite	1000	2	10.43	24.15		
Calamine - Graphite	1025	2	60.15			
Calamine - Graphite	1050	2	98.19			
Calamine - Graphite	1100	2	99.44			

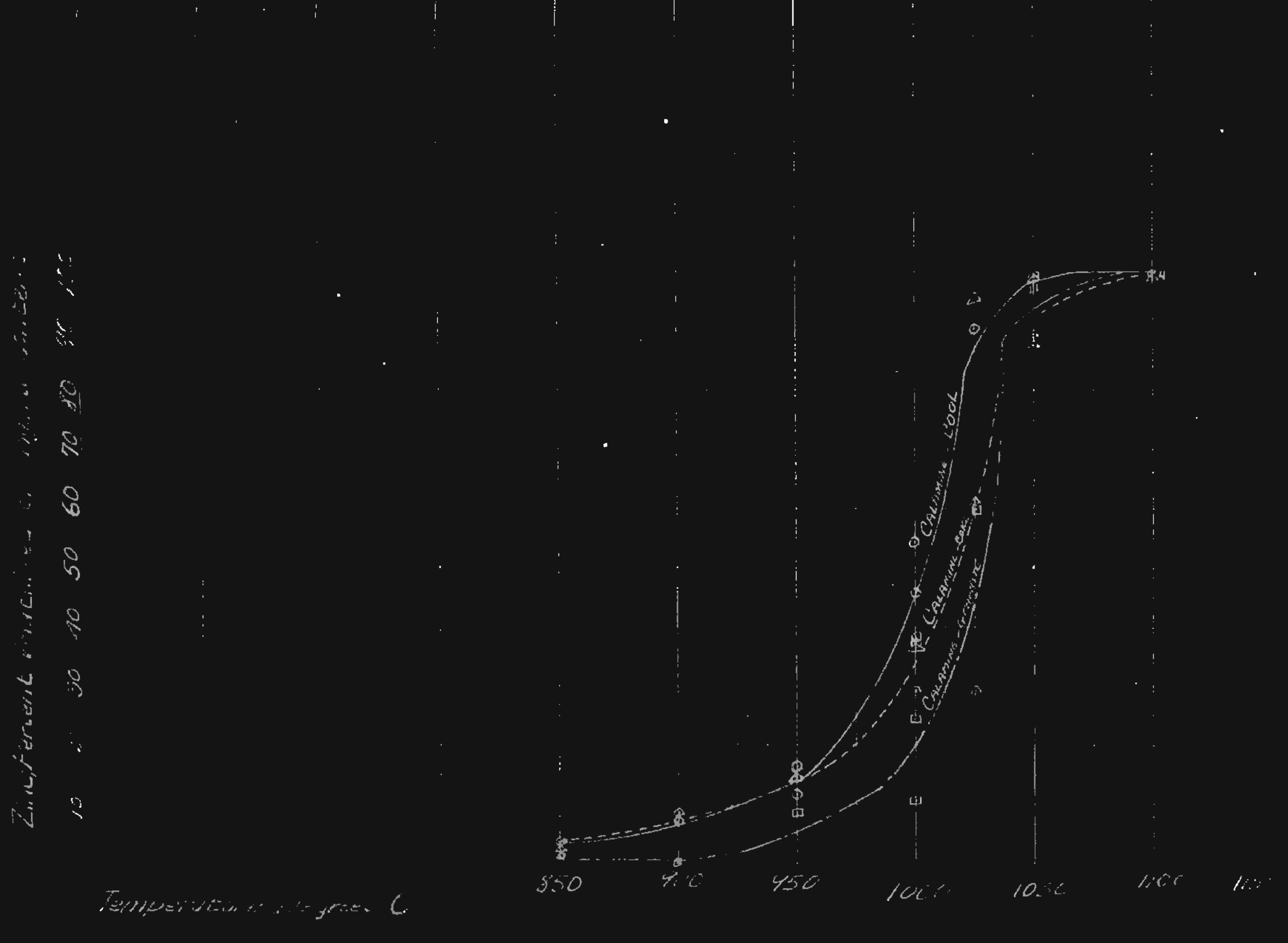
Calamine 100%
Calamine 50%
Calamine 25% Zinc 75%
450
1050

Figure 4.

Curves showing the effect of temperature on the rate of reduction of calamine by carbon.

Time - Two hours in each experiment.

The reduction of zinc began at some temperature below 850° C., and increased with increasing temperature, slowly at first but rapidly with rising temperature. After rising rapidly at these higher temperatures, the curves as shown in Figure 4, bend over to the right, indicating that the rate of reduction increases less rapidly at still higher temperatures; it is evident, however, as in the case of the experiments with zinc ferrite, that this retardation on the reduction rate is due to the fact that in the experiments at the higher temperatures the zinc was nearly completely volatilised in two hours or less, and the reduction necessarily slowed down, because of the much diminished amount of zinc present.

The accuracy of the experimental results is not sufficient to permit the extrapolation to give the exact temperature at which the reduction begins, but it is evident that it begins at some temperature below 850° C.

Effect of Temperature Upon the Rate of Reduction of Willemite with Carbon.

Three series of experiments were carried out to determine the effect of temperature on the rate of reduction of willemite. The three series were with mixtures of willemite with antrhacite coal, coke, and graphite as reduction material, respectively. Each series consisted of several individual experiments at small temperature intervals, from the temperature at which the amount of zinc volatilized was negligible to the temperature at which nearly all the zinc was volatilized. In all the experiments the furnace was held constant at the desired temperature for two hours. The percentages of the original zinc that was volatilized in two hours at the various temperatures are shown in Table IV and Figure 5.

Each of the small circles represents an individual experiment with willemite and anthracite coal, while the triangles and squares represent the individual experiments with willemite with coke, and graphite, respectively. As shown by the curves, volatilization of zinc begins at some temperature below 950° C., and the rate of volatilization increases with increasing temperature, slowly at first but very rapidly at higher temperatures. After rising rapidly at these temperatures, the curves in the figure bend over to the right, for the same reason that has been explained in the description of the experiments with zinc ferrite and calamine.

Table IV.

Effect of Temperature Upon Rate of Reduction of Willemite by Carbon.

Materials	Temperature Degrees C.	Time Hours	Zinc Volatilized Per cent of Original Content		
Willemite - Coal	850	2	1.18		
Willemite - Coal	900	2	0.00		
Willemite - Coal	950	2	12.97		
Willemite - Coal	1000	2	39.29	62.40	
Willemite - Coal	1050	2	92.04		
Willemite - Coal	1100	2	100.0		
Willemite - Coke	850	2	0.00	0.51	
Willemite - Coke	900	2	2.39	2.064	
Willemite - Coke	950	2	7.07	4.80	
Willemite - Coke	975	2	10.75		
Willemite - Coke	1000	2	15.49	33.46	22.47
Willemite - Coke	1050	2	99.20	69.02	64.50
Willemite - Coke	1100	2	80.60	75.20	85.80
Willemite - Graphite	850	2	0.00		
Willemite - Graphite	900	2	8.20	3.84	
Willemite - Graphite	950	2	7.62		
Willemite - Graphite	1000	2	23.60	34.19	
Willemite - Graphite	1050	2	86.00		
Willemite - Graphite	1100	2	66.32	97.70	

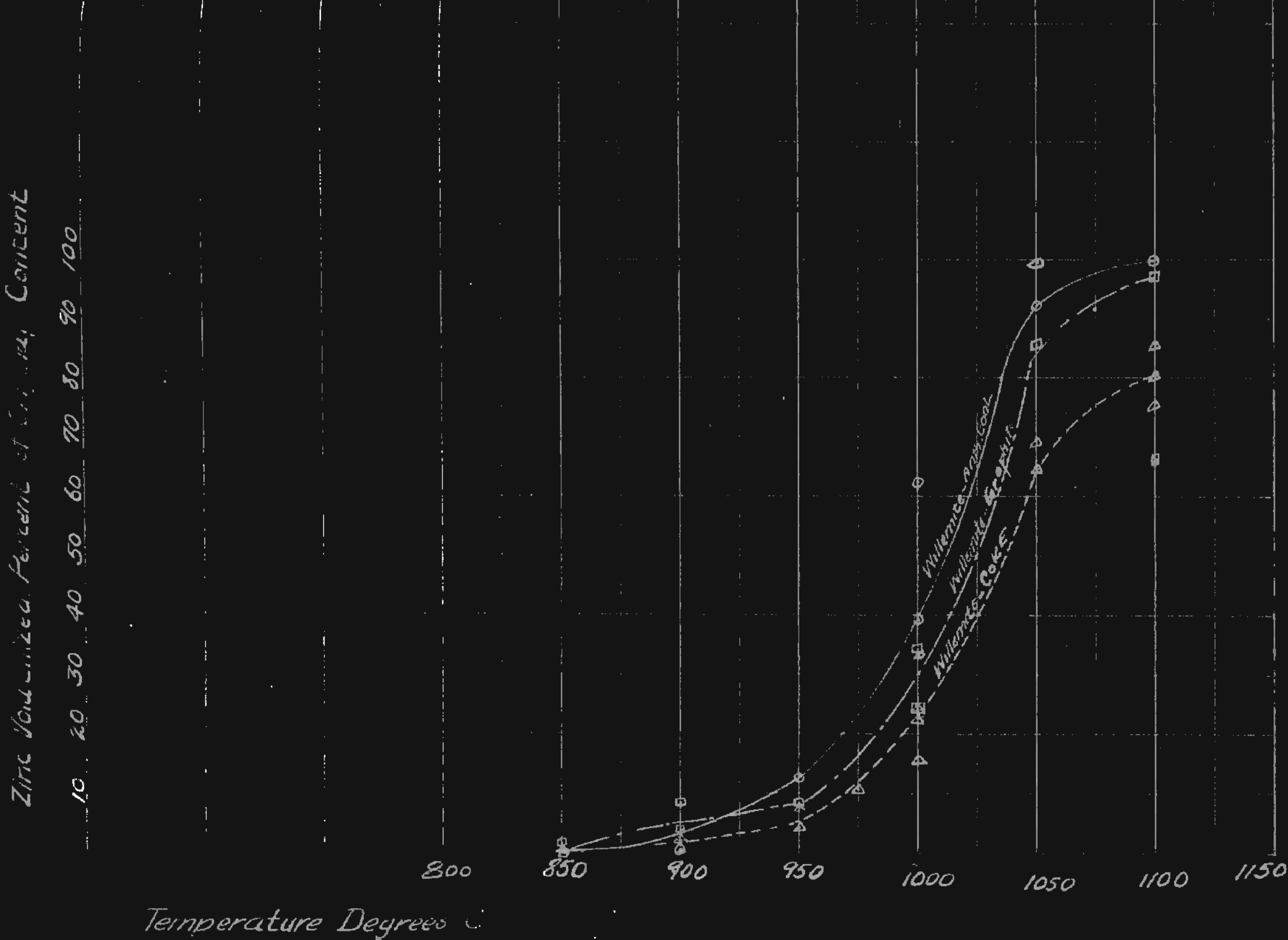
Zinc Volatilized Percent of Total Content
10
20
30
40
50
60
70
80
90
100
800
850
900
950
1000
1050
1100
1150
Temperature Degrees C
Willamette Anthracite
Willamette Briquets
Willamette Coke

Figure 5.

Curves showing the effect of temperature on the rate of reduction of willemite by carbon.

Time - Two hours in each experiment.

It is probably safe to assume the shape of the curves of willemite with anthracite coal and with graphite is due largely to the effect of temperature up to 80 per cent reduction, while for willemite and coke the point is close to 65 per cent reduction. Above this point the bending over of the curves to the right is due to the much diminished amount of zinc present.

S U M M A R Y.

In the first part of this thesis the information found in the literature concerning the physical and chemical properties and formation of zinc ferrite, calamine, and willemite has been reviewed.

In the second part an investigation of the effect of various factors upon the rate of reduction of zinc ferrite, calamine, and willemite, by carbon, has been described. In summary of this investigation it may be said that the rate of reduction of zinc ferrite, willemite, and calamine, by carbon, increases very rapidly with rising temperature. The relation is very similar to the relation between temperature and the rate of reduction of zinc oxide, as shown by the investigation of G. A. Zeller, previously referred to, but the experimental results obtained were not sufficiently consistent to allow the relation to be as definitely stated as was the case in Zeller's investigation. Apparently, as indicated by comparing the results of this investigation with that of Zeller, zinc ferrite is more easily reducible than zinc oxide, and willemite and calamine are more difficultly reducible than zinc oxide. The easy reducibility of zinc ferrite is surprising, as most metallurgists have previously held that it was more difficultly reducible than zinc oxide.

The decrease in the rate of reduction of zinc ferrite with increasing time of distillation is similar to that found by Zeller in the case of zinc oxide. As was to be expected, anthracite was found to be a better reducer than either coke or graphite for both zinc ferrite and the zinc silicates. Graphite was apparently a better reducer for the zinc silicates than was coke; this is contrary to what would be expected, as coke is the better reducer for zinc oxide.

A C K N O W L E D G E M E N T S.

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